

ELECTROCHEMICAL CAPACITANCE OF NO-TREATED ACTIVATED CARBONS

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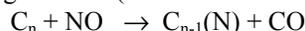
Abstract

Nitrogen-doped activated carbon was prepared by NO treatment of conventional activated carbon fibers (ACF). The NO treatment was carried out by heating at 800°C in He carrier gas containing 2000 ppm NO. Pyridine, pyrrole, or quaternary-like nitrogen was detected by XPS analysis. The NO treatment slightly promoted the gravimetric and volumetric capacitance and the specific capacitance per surface area in the conventional organic electrolyte. The cyclic voltammetry revealed that the electrochemical behavior around p.z.c was changed by the NO treatment. This suggests that the nitrogen doping modified the dielectric character of the activated carbon to influence the capacitance properties.

Introduction

“Electric double layer capacitor” (EDLC) is the electric energy storage system based on non-faradaic process (electrosorption) in an electric double layer on porous carbon electrodes, which has been already used as memory back-up device because of its high cycle efficiency and the long cycle life. Recently, EDLC has been also expected as the power source for hybrid electric vehicle because of its higher power density (larger than 1000 W kg⁻¹ or 1000 Wdm⁻³) and fast charge-discharge ability. The commercialized electrode materials for EDLC are activated carbons. The high capacitance (100 ~ 200 Fg⁻¹) is derived from high specific surface area (>1000 m²g⁻¹) with many micropores. Many researchers have investigated the correlation of the pore structure and the capacitance. The increment of the surface area or the control of the pore size distribution of activated carbons is known to be effective in improving the capacitance of EDLC. However, it is difficult to realize more improvement of the capacitance by only these above ways. Therefore, the other factors should be focused. For example, heteroatom doping such as nitrogen or boron doping to carbon has been proposed as a break through. Nitrogen-enriched carbons show high capacitances (Shiraishi et al. 2004; Frackowiak et al. 2006; Kodama et al. 2006). The following possibilities can be understood as the reasons for the capacitance enhancement by the nitrogen doping. (1) Wettability improvement due to polarity increase on carbon surface, (2) Redox capacitance contribution that is related to the electrochemical activity of nitrogen functionality like conductive polymer, (3) Increase of space charge capacitance, which consists the series capacitance circuit with the Helmholtz capacitance at the interface of carbon and electrolyte. However, the details have not been clarified yet.

In generally, the heteroatom-enriched carbons are prepared by the replica method of heteroatom-enriched polymer. This is an expensive method and difficult to realize higher surface area than 1500 m²g⁻¹ comparable to that of conventional activated carbons. Nitrogen monoxide (NO) is known to react carbonaceous materials to produce nitrogen-containing carbons, which can be explained by the following reaction (Suzuki et al. 1994).



, where C_n is carbon surface, C_{n-1}(N) is nitrogen-containing carbon surface. This reaction can be applied to nano-porous carbons such as activated carbons. In this paper, we report the capacitance properties of the nitrogenous activated carbon prepared by the NO reaction with conventional activated carbons.

Experimental

Activated carbon fibers (ACF), which were prepared by the carbonization and the steam-activation at 800°C of phenolic resin fibers, was used as the start material. NO reaction of the ACF was carried out at 800 °C in He gas containing 2000 ppm NO. The test electrodes (disk shape, 13 mm diameter, ~ 30 mg) were prepared by pelletizing the mixture of the activated carbons, conductive additive (acetylene black), and PTFE-based binder, of which the mixing ratio was 85:10:5 in weight %. The BET specific surface area, pore volume, and mean micropore width were calculated by the nitrogen adsorption isotherm at 77K. Propylene carbonate solution containing 0.5 moldm⁻³ (C₂H₅)₄NBF₄ was used as electrolyte. The test electrode immersed in the electrolytes was degassed under reduced pressure. The cyclic voltammetry and the chronopotentiometry were carried out with a standard three-electrode cell, which was composed of the counter electrode (ACF cloth) and a reference electrode (Li/Li⁺) with glass filter as the electrolyte separator. The double layer capacitances were calculated from the slope of the chronopotentiograms (40 mA g⁻¹, 2 ~ 4 V vs. Li/Li⁺) (Shiraishi et al. 2002). The charge-discharge cycle test was carried out using two-electrode system with Al-body.

Result and Discussion

Chemical composition and Pore Structure

The chemical state of doped nitrogen and surface atomic ratio of nitrogen / carbon (N/C) of NO-reacted activated carbons were characterized by N1s XPS analysis (**Figure 1**). The main peak attributed to pyridine-like nitrogen was observed around 399 eV. The peak should around 400 eV can be assigned to pyrrole-like or quaternary-like nitrogen. The ratio (N/C) was 0.3~0.4, depending on the duration of the reaction time. The ratio well corresponded to the chemical composition characterized by combustion elemental analysis. This suggests that nitrogen was doped to the internal part of activated carbons,

Table 1 shows the pore structure of the activated carbon characterized by nitrogen adsorption isotherms. Comparing the pore structure before and after the NO reaction, significant difference was not observed for the surface area, the pore volume, and the mean micropore width. The experimental condition of these NO reaction can be considered to be mild, which is suitable to discuss the nitrogen-effect on the capacitance.

Electrochemical Properties

Figure 2 shows the cyclic voltammograms of the pristine activated carbon (p-ACF) and the NO-treated one (NO-ACF120). The shape of both of the voltammograms was butterfly-like shape, which is usually observed for well-activated carbons in organic electrolyte for EDLC. The depression around 3V vs. Li/Li⁺, which corresponds to p.z.c, was smoother for NO-ACF120 than that for p-ACF. Considering the little change in the pore structure by the NO reaction, this result suggests that nitrogen-doping influenced the dielectric structure of the internal surface of the activated carbons.

Table 2 shows the capacitance of ACF and NO-treated ACF (NO-ACF120 or NO-ACF240). The gravimetric capacitance (C_g) was increased by the NO treatment. But, these data is difficult to discuss the effect of the nitrogen-doping since the C_g is related to the surface area shown. The specific capacitance per surface area ($C_s = C_g / S_{BET}$) suggests the effect of the nitrogen-doping on the capacitance, however, it was not much prominent than expected.

The cycle-performance of the activated carbons is important for the practical use. The dependence of the capacitance on charge-discharge cycle was summarized in **Figure 3**. The discharge capacitance of the pristine ACF decreased with increasing cycle numbers, especially, the capacitance decline was significant at the most severe condition (3V, 70°C). However, the NO-treated ACF showed more stable cycle-performance, compared with the pristine ACF. This result suggests that the nitrogen-doping is very effective for the cycle-performance. We are now investigating the surface chemical condition such as nitrogen condition after the cycle test.

Table 1. NO-reaction time (2000 ppm NO gas, 800°C), BET specific surface area (S_{BET}), mesopore volume (V_{meso}), micropore volume (V_{micro}), and mean micropore width (w_{micro}).

Sample	NO reaction time [min]	S_{BET} [m^2g^{-1}]	V_{meso} [mlg^{-1}]	V_{micro} [mlg^{-1}]	w_{micro} [nm]
p-ACF	-	2040	0.43	0.85	1.18
NO-ACF120	120	1970	0.43	0.82	1.20
NO-ACF240	240	2160	0.56	0.90	1.22

Table 2. BET specific surface area (S_{BET}), gravimetric capacitance (C_g), volumetric capacitance (C_v), and specific capacitance per surface area ($C_{SA} = C_g / S_{BET}$).

Sample	S_{BET} [m^2g^{-1}]	C_g [Fg^{-1}]	C_{SA} [μFcm^{-2}]	C_v [Fdm^{-3}]
p-ACF	2040	113	5.5	56
NO-ACF120	1970	113	5.7	58
NO-ACF240	2160	121	5.6	59

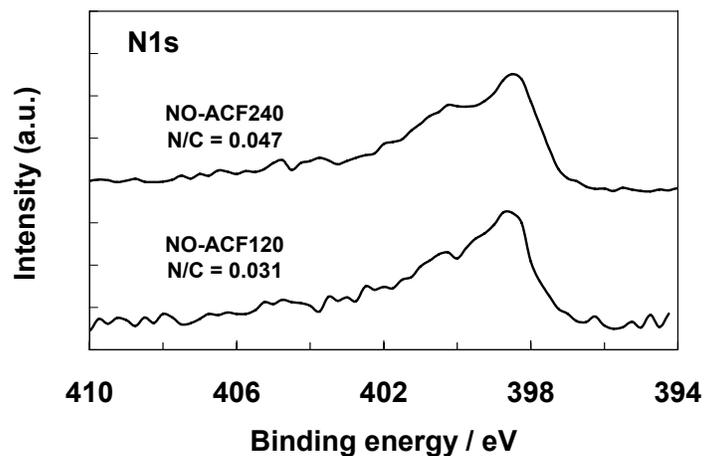


Figure 1. N1s XPS spectra of NO-ACF120 and NO-ACF240.

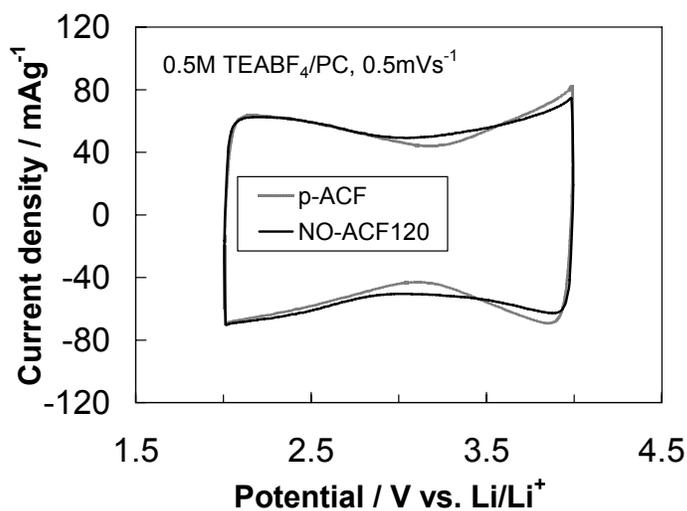


Figure 2. Cyclic voltammograms (0.5mVs^{-1}) of p-ACF and NO-ACF120 in 0.5 M $(\text{C}_2\text{H}_5)_4\text{NBF}_4$ / propylene carbonate (TEABF₄/PC).

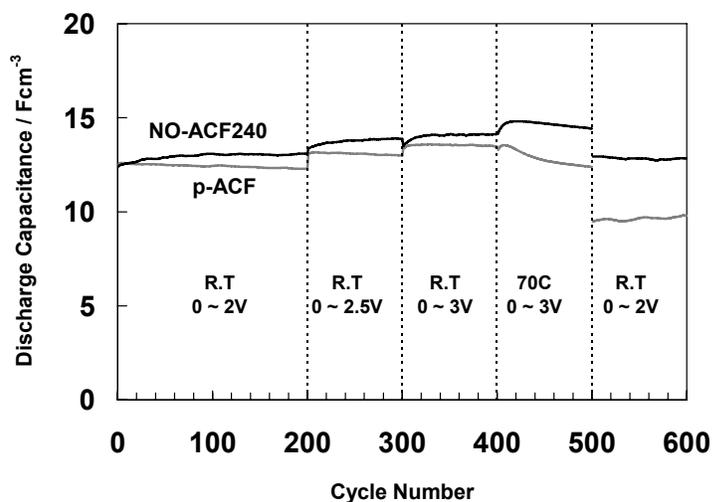


Figure 3. Capacitance-dependence (two-electrode cell, galvanostatic, 1.2 mA) on charge-discharge cycle for p-ACF and NO-ACF120 in 0.5 M TEABF₄/PC. The applied voltage and temperature : 0~2V at room temperature (R.T.) (1~200 cycle No.), 0~2.5V at R.T. (201~300 cycle No.), 0~3V at R.T. (301~400 cycle No.), 0~3V at 70 °C (401~500 cycle No.), and 0~2V at R.T. (501~600 cycle No.).

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